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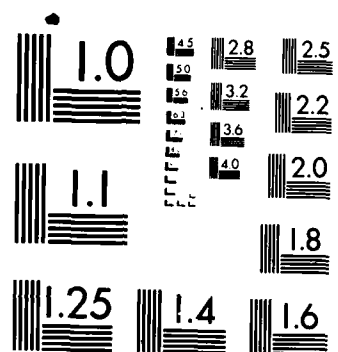
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Microvoltammetric electrodes, electrodes of micrometer dimensions, have opened many new domains for electrochemical investigations. Depending upon the experimental conditions, these include increased temporal resolution, increased current density, and decreased sensitivity to the effects of solution resistance. In the last three years, we have experimentally shown that dramatic improvements in electrochemical data can be obtained with these (cont.)			

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electrodes. A number of different areas have been investigated with the emphasis on obtaining data that is inaccessible with electrodes of conventional size. Successfully completed projects include measurement of transient electrogenerated intermediates on a microsecond time scale, the use of electrochemistry in highly resistive media such as solutions of benzene, and a characterization of the mass transport processes operant at these electrodes. In addition, the analytical opportunities of microvoltammetric electrodes have been explored, especially as liquid chromatographic detectors.

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MICROVOLTAMMETRIC ELECTRODES

FINAL REPORT

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#### 4. Body of Report

##### A. Statement of the problem studied

The research proposal entitled "Microvoltammetric Electrodes" which was jointly funded by the U.S. Army Research Office and the National Science Foundation was directed at exploring the wide new possibilities in electrochemistry offered with microvoltammetric electrodes. The specific research plan was to simplify the method of construction of microvoltammetric electrodes, to explore the use of these electrodes under steady-state conditions, especially in resistive solutions and under hydrodynamic conditions, to develop fast scan voltammetry, and to investigate the properties of carbon electrodes. Progress has been made in each of these areas and will be summarized in the following section. The majority of these results have been published in the scientific literature. This summary follows the outline used in the original research plan.

##### B. Summary of the most important results

###### 1. Construction of Electrodes.

At the time the original research proposal was written, most of our experience in the construction of microvoltammetric electrodes was with the use of carbon fibers inserted in a glass pipette. These electrodes have been shown to be ideal for in vivo use, but they are fragile, and thus are not suitable for routine electrochemical investigations. Therefore, in the original research plan we proposed to build electrodes with a large insulating area surrounding a small disk-shaped electrode. The rationale was that this type of electrode would be easy to resurface, and could be used in a fashion similar to electrodes of conventional size. In fact, we have demonstrated that it is very easy to seal gold or platinum wires in soft glass simply using a bunsen burner flame (1). Electron microscopy shows that there is a good seal between the glass and the electrode material, and these have been used routinely in our lab for the last two years. Construction of carbon microvoltammetric electrodes by this technique proved to be more troublesome -- the carbon fiber tends to evolve  $\text{CO}_2$  when heated, and thus a good seal cannot be obtained. However, we have successfully made carbon microvoltammetric electrodes in a large insulating material using epoxy (1). More recently, we have found that carbon fibers can be sealed in glass when this is done in a nitrogen atmosphere.

In the original proposal we suggested several ways in which electrodes could be constructed which would exhibit the steady-state electrochemical properties of microdisk electrodes, but would yield large and more easily measured currents. An array of carbon fiber disk electrodes has been demonstrated as a means to achieve the advantages of microvoltammetric electrodes while maintaining easily measured currents (2). Recently we have examined the properties of microcylinder and line electrodes (3). We have found that the current-time relationships of faradaic processes at microcylinder electrodes can be predicted by the equations derived for heat flux to a cylinder. An estimation of the magnitude and temporal properties of the measured current at a band electrode can be obtained with equations derived for a hemicylinder geometry. In addition, mercury microelectrodes have been constructed (4).

## 2. Steady-State Voltammetry.

When microvoltammetric electrodes were first developed, it was recognized that one of their most unusual features was that, at conventional scan rates ( $< 100 \text{ mVs}^{-1}$ ), voltammograms were totally time independent. This observation led to the proposal that this unique feature could be used to investigate several different aspects of electrochemistry.

### a. Voltammetry in resistive solutions.

Because of the very low currents measured with disk-shaped microvoltammetric electrodes, we proposed that electrochemistry would be viable in solutions containing very small amounts of supporting electrolyte. We also proposed that this would be most easily done under conditions where steady-state voltammograms are obtained. This has been experimentally confirmed (1). We have found voltammograms of the oxidation of ferrocene in acetonitrile are virtually undistorted, even when the supporting electrolyte is one-tenth the concentration of the depolarizer. We have also investigated voltammetry in a number of solvents not normally used in electrochemical studies (5). These included benzene, chlorobenzene, tetrahydrofuran, and dimethoxyethane. In fact, we were able to show that with the exception of benzene, very fast voltammetry also could be performed with minimal distortion in these solvents.

### b. Microelectrodes with convection.

Since microvoltammetric electrodes show time-independent behavior at relatively long times, we proposed to investigate the sensitivity of the current at these electrodes to solution convection. This was accomplished with an array of carbon fiber disks arranged in a channel detector suitable as a liquid chromatographic detector (2). This type of detector was shown to be advantageous over a glassy carbon electrode of conventional design. The improvement in signal-to-noise ratio was ascribed to the in sensitivity of the array electrode to faradaic currents arising from impurities in solution, and which are modulated by fluctuations in the flow rate. This enabled the determination of compounds, while maintaining favorable signal-to-noise ratios at potentials near the positive potential limit for carbon electrodes.

We have also shown that the low value of the capacitance of the carbon fiber array facilitates the use of rapid scan voltammetry during its use as a liquid chromatographic detector. This enables the identification of a compound eluting from a chromatographic column by voltammetric properties as well as its characteristic retention time (6). In related research, we established that liquid chromatography with electrochemical detection is suitable for the detection of polyaromatic hydrocarbons and polyaromatic amines, substances of environmental importance (7).

## 3. Very Rapid Electrochemistry.

A particularly unique feature of microvoltammetric electrodes, that we have demonstrated under the existing grant, is their capability for use in fast scan voltammetry. At scan rates above  $200 \text{ V s}^{-1}$ , voltammograms at microvoltammetric electrodes exhibit the characteristics of linear diffusion. The reduced double layer capacitance and  $iR$  drop permits scan rates

up to  $20,000 \text{ V s}^{-1}$  to be obtained with minimal distortion (1). We have exploited these features to investigate electron transfer rates for a number of aromatic compounds in nonaqueous solution using cyclic voltammetry. Although this technique has the capability of measuring rates exceeding  $20 \text{ cm s}^{-1}$ , compounds which exhibit such fast rates have not yet been found. We have also demonstrated the use of ultrafast voltammetry in the determination of rapid chemical reactions which follow electron transfer (5). Under conditions where the scan rate is sufficiently fast to outrun chemical reactions, chemically reversible voltammograms are obtained, and values of the formal potential can be observed. In conjunction with Professors Christian Amatore and Jay Kochi, we have measured the redox potentials for the formation of the radical cation of a number of different aromatic hydrocarbons (8). In addition, we have used this technique to determine the disproportionation equilibria for the radical cation of diphenylanthracene in a variety of solutions (5).

#### 4. Carbon Electrodes.

The rationale for an investigation of the properties which affect electron transfer at carbon electrodes was based on the fact that carbon had been our most successful substrate for making microvoltammetric electrodes. However, electron transfer reactions are generally slow at carbon electrodes, and thus we needed methods to accelerate these rates so that we could employ the fast voltammetric techniques. One method which we found particularly useful was the heat treatment of glassy carbon (9). However, the most useful method that we have found is to employ an electrochemical pretreatment (10). Our research does suggest that for highly-charged molecules, the carboxyl groups on the surface of carbon can affect the electron transfer rates (11). For these types of molecules, various pretreatments are proposed to eliminate this effect.

#### Conclusions

Thus, it can be seen that the research of the last three years has resulted in significant advances in microvoltammetric electrode construction, and their use in electrochemical experiments. Their unique properties have allowed us to make measurements in domains that are normally inaccessible to electrochemical techniques. In addition, the methodology we have developed is sufficiently simple that it can be used in a wide number of other laboratories.

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**D. List of all participating scientific personnel showing any advanced degrees earned by them while employed on the project**

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